Magnetic Ordering in a Quasi Two-Dimensional Planar Ferromagnet: $CoCl_2$ in Graphite

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The Kosterlitz-Thouless [1] theory describes the static properties of a wide range of two-dimensional (2 D) systems with xy symmetry. Following Mermin and Wagner [2] in the statement that no true long-range order may exist in 2D xy system down to $T = 0$, Kosterlitz and Thouless showed that topological order instead of long range order may exist below a critical temperature (T_{KT}). The topological order is characterised by a state of bound vortices of opposite helicity, and a phase transition to a phase of short range order takes place when these vortices unbind and move freely about.

One suitable test system for a KT type phase transition is found in stage 2 $CoCl_2$-graphite intercalation compound (GIC), which is a layered Heisenberg antiferromagnet with pronounced xy spin anisotropy. The Hamiltonian of this system can be written as:

$$H = -J \sum_{<ij>} \vec{S_i} \cdot \vec{S_j} + J_A \sum_{<ij>} S_i^2 S_j^2 + J\prime \sum_{<im>} \vec{S_i} \cdot \vec{S_m} + h_6 \sum_i \cos(6\phi)$$

Where J is the in-plane exchange interaction, J_A is the single spin anisotropy parameter. $J\prime$ takes care of interplanar interaction, and h_6 represents the 6-fold anisotropy field. In stage 2 $CoCl_2$ - GIC, J_A /J = 0.45, $J\prime/J \approx 10^{-4}$, and $h_6 \approx 50\ O_e$, which represent suitable parameters for qualifying as a quasi-2D system with strong xy symmetry.

Assuming a vortex state, the elastic structure factor $S(q)$ below T_{KT} is characterized by a power law line shape $S(q) \propto q^{-2+\eta}$ representing the algebraic decay of the pair correlation function $g(r) \propto r^{-2+\eta}$, instead of the classic δ-function line shape ($S(q) \propto \delta(q)$) resulting from true translational long-range order. Above T_{KT}, the vortices unbind and the topological order goes over into short range order. However, the correlation length ξ and the susceptibility χ do not simply diverge in a power law fashion within the critical regime close to T_{KT} but rather exhibit exponential divergencies:

$$\xi \propto exp(b/\sqrt{t}), \quad \chi \propto exp[2 - \eta)b/\sqrt{t}]$$

with $|t| = |1 - T/T_c|$.

Susceptibility studies by Murakami and Matsuura [3] on stage 2 $CoCl_2$ - GIC showed a maximum at about $T_l = 8.5K$ and a shoulder at about $T_u = 9.5K$. The magnetization reaches a maximum at T_u, drops to a saddle point at T_l, and raises again below T_l, following the shape of a normal order parameter. These measurements were interpretated in the following way. For $T < T_l$, the spins may lock into the symmetry breaking field provided by the local crystal field, yielding long-range in-plane ferromagnetic order. For $T_l < T < T_u$ bound vortices may prevail, while for $T > T_u$ those vortices may unbind. Thus, T_u may be reconciled with T_{KT}, while T_l would correspond to a spin locking transition as predicted by José et al. [4].

Detailed neutron scattering investigations of the magnetic phase transitions in stage $2-CoCl_2$ - GIC have recently been carried out by Wiesler et al. [5-7]. Two main scattering experiments shall be discussed here. The first concerns a scan along the c* direction, probing the 2D ferromagnetic (FM) in-plane correlation as well as the 3D antiferromagnetic (AFM) out-of-plane correlation. In the second experiment, scans across the ridge along the c* direction were carried out, avoiding the antiferromagnetic Bragg-points. Those scans are particular useful for analyzing the critical regime with respect to line shapes, correlation functions, and critical exponents.

Scans along the c* direction revealed that for $T < T_l$ an AFM coupling between neighboring Co^{2+} planes occurs, with an intensity increase of the AFM Bragg peaks following the shape of an order parameter. The width of the AFM Bragg-peaks shows, however, considerable broadening, indicating that the AFM correlation is of very short range. In fact, the correlation length ξ, perpendicular to the planes saturates at about 22 Å at 4 K, corresponding to not more than 2 to 3 Co^{2+} layers. Although the AFM correlation remains of short range down to the lowest temperature, its origin are not short range order type spin fluctuations, but rather an incomplete ordering hindered by the domain structure of the intercalate islands as well as the non-perfect AFM spin alignment in neighboring intercalate planes [5]. The AFM Bragg peak is superimposed on a 2D ridge-like intensity streching along c*. This ridge intensity is due to FM in-plane correlation with lacking AFM out-of-plane correlation. The 2D FM intensity also follows the temperature dependence of an order parameter, but drops to zero at the higher temperature T_u. Thus, between T_l and T_u there is a temperature window of about one degree width where only 2D FM correlation is present. It will be in this window where a bound vortex state may exist, and this will be discussed in the next paragraph. As to the hindered AFM correlation, it is evident that if the out-of-plane correlation could be increased, the intensity of the 2D FM correlation (the ridge like intensity along c*) would decrease proportionally.

The scans crossing the ridge were taken at positions which only probe the 2D in-plane FM correlation. Scans were recorded with decreasing temperature from 40 K to 5 K. For $T > T_u$, the scattering function exhibits a Lorentzian line shape due to SRO spin correlation. For $T \leq T_u$, a long-range component starts to grow in intensity. For all temperatures the line shape can be described by the superposition of a Lorentzian and δ-part:

$$I(q) = M^2(T)\delta(q) + \frac{I_o}{(1+(\frac{q}{\chi_{\|}})^2)^p}$$

Here M(T) represent the order parameter of the long range order part, and $\kappa_{\|} = 1/\xi_{\|}$ is the inverse correlation length of the in-plane spin structure. The intensity I_o is porportional to the generalized susceptibility χ. Fitting of the data with the expression above showed again that the 2D FM correlation starts at T_u. The intensity I_o of the SRO part follows rather closely the shape of the bulk susceptibility as determined by Murakani and Matsuura (see Fig. 1) [3].

Detailed analysis of the data showed [8] that the correlation $\xi_{\|}$ and the susceptibility $I_o \propto \chi$ fail to diverge close to T_u and that they appear not to follow the exponential

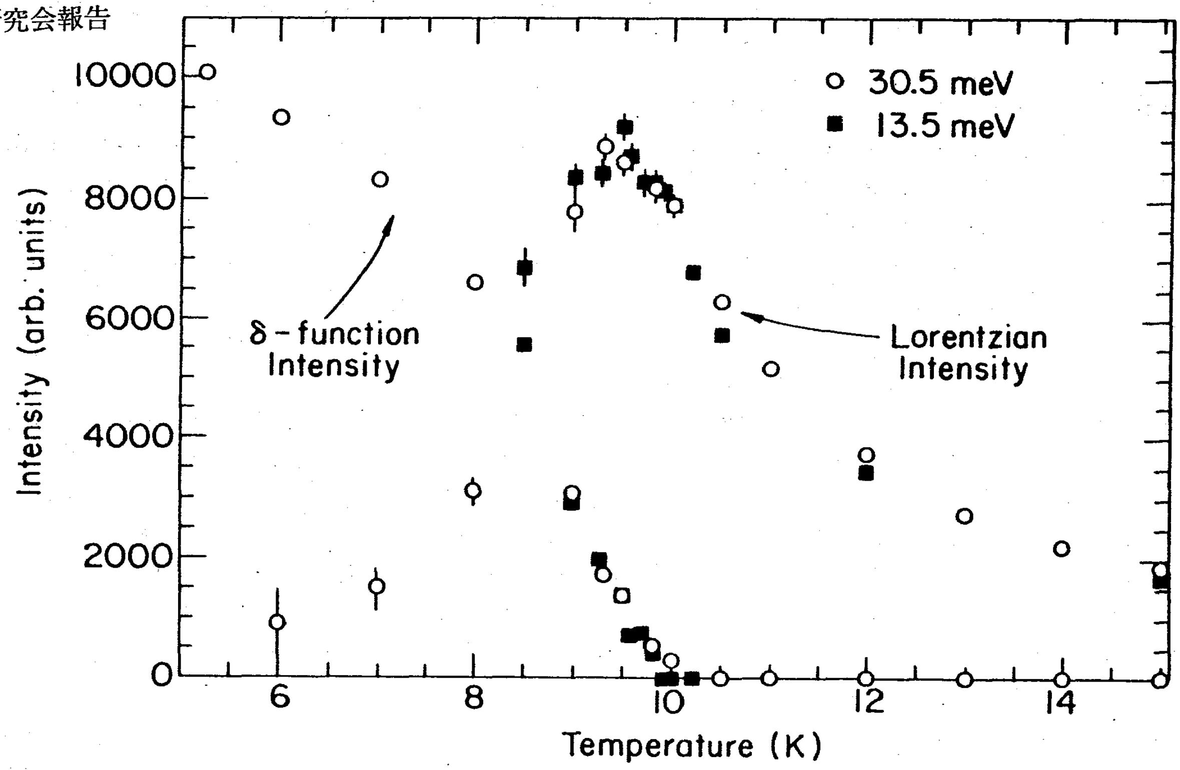

Fig. 1 Intensities of the Lorentzian and δ-function part as a function of temperature. The Lorentzian term, showing a peak at T_l and a shoulder at T_u agrees with susceptibility measurements by Murakami and Matsuura [3]. The δ-part behaves qualitatively like a normal order parameter (from Ref. 8).

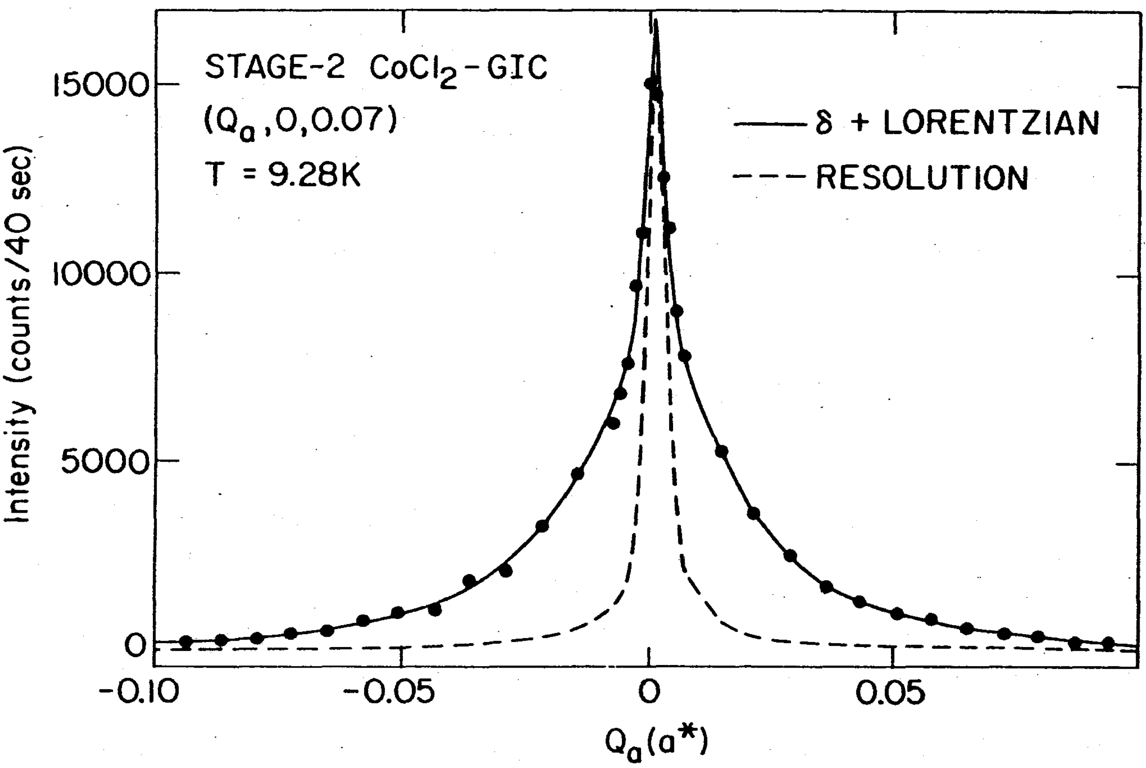

Fig. 2 Critical scattering at 9.28 K, between T_l and T_u. The solid line corresponds to a fit of the data points to a δ-function and a Lorentzian line shape, both convoluted with the instrumental width function (dashed line) (from Ref. 8).

behavior as predicted by the KT theory. Moreover, the line shape of the scattering function S(q) in the temperature regime between T_l and T_u does not exhibit the expected power law behavior. Instead it can be described by the superposition of a δ- function and a Lorentzian line shape (Fig. 2). In this respect, the 2D FM regime in stage 2 $CoCl_2$ - GIC appears not to conform to a KT state. It is more likely that for $T \leq T_u$ the spins lock into a particular symmetry breaking field causing long-range translational order instead of topological order. In other words, the present elastic data in the critical regime $T_l < T < T_u$ can not be reconciled with the presence of a vortex state. There remains the slight possibility that in the 2D FM regime the pair correlation function breaks up into two parts: The first part for small distances would have the usual exponential behavior whereas at larger distances the pair correlation would change over into an algebraic decay. The Fourier transform, i.e. the scattering function, would then be composed of a Lorentzian part plus a part with power law line shape. This line shape would be very hard to distinguish from a Lorentzian and δ- function line shape. However, since no change in the quality of the line shape occurs at T_l, we believe that already for $T_l \leq T \leq T_u$ the proper description of the scattering function is indeed the superposition of a Lorentzian and a δ-function.

One remaining question warrants some explanation. Why does the long-range FM in-plane correlation, which occurs at T_u, not immediately trigger a $2D \rightarrow 3D$ cross-over effect as observed in many other quasi 2D systems. In other words, why is the onset of the 3D AFM correlation perpendicular to the planes offset from T_u by about 1 K. In general, no matter how weak the interplanar interaction J' is, the divergence of the in-plane correlation $\xi_{\|}$ at T_c always drives a $2D \rightarrow$ 3D cross-over according to

$$J_{eff} = J'(\frac{\xi_{\|}}{a})^2,$$

where a is the in-plane lattice parameter.

In the present case of stage 2 $CoCl_2$ - GIC the in-plane correlation length $\xi_{\|}$ remains limited to the size of the $CoCl_2$ islands in graphite, which are on the order of 800 Å. Thus, a transition $\xi_{\|} \rightarrow \infty$ does not take place. In this case, Murakami and Matsuura [3] pointed out that it may be energetically more favorable to arrange FM islands in a random fashion on top of each other because of the gain in entropy, and only at lower temperatures, when the entropy term in the free energy loses weight, ordering of the islands in the third dimension takes place. This interpretation sheds new light on the transitions taking place at T_u and T_l. In the past, it was conjectured that T_u is characterized by the onset of a KT type vortex state and that at T_l the spins lock into a symmetry breaking field causing true long range order. The present neutron scattering experiments, however, show that long range FM in-plane order already appears at T_u. Since the FM correlation is limited to the island size of the $CoCl_2$ intercalate islands, the configurational entropy S of the islands becomes an important factor in the energetics of the system. AFM order perpendicular to the planes is then achieved when the configurational entropy and the interplanar interaction J' balance, characterizing $T_l = J'/S$.

As mentioned above, below T_l the interplanar AFM order remains rather imperfect and is limited to about 2 to 3 layers. It is important to note that this short correlation length should not be considered as short range order correlation but as hindered 3D long range order. The latter being caused by incomplete AFM alignment of the spins in neighboring planes and by imperfect arrangement of the islands on top of each other.

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